SYMMETRIES OF HIGHER ORDER AND THEIR INVARIANCE

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ABSTRACT. If the equation of entropy-generation, considered as phenomenological law, is taken as the starting-point, general symmetry-relations, which are generaliations of Onsager relation, can be obtained. For this, the fact that generalised forces are differences or gradients of some thermodynamic quantities is to be fully utilised. Then, by simple and straightforward calculations, these symmetry-relations can be seen to be invariant under the general group of linear transformations of forces or fluxes. So, these symmetry-relations are natural laws as the Onsager reciprocal relation.

INTRODUCTION

In the linear theory of irreversible phenomenae, the Onsager reciprocal relation plays a very important role (Onsager 1931, de Groot, 1951) and is considered as a fundamental law. But it is seen that the linear theory is not suitable in some cases, particularly when the chemical reactions are important in the irreversable processes (de Groot, 1951). Some attempts have been made to formulate and develop a non-linear theory. In this theory, the symmetry relations of higher order are important.

Here, symmetry-relations of higher order have been deduced simply from the well-known fact that the thermodynamic generalised forces are differences or gradients of some thermodynamic quantities, (generally intensive variables). The equation of entropy generation, taken in the usual form, is considered as a basic law and the closed study of its implications has been made. From this study the invariance of symmetry-relation of higher order under a general group of linear transformations of forces or fluxes follows simply and straight-forwardly.

BASIC NOTIONS AND THEIR SIGNIFICANCES

As already stated, a generalised force, X^μ, is the difference of some thermodynamic quantity x^μ like temperature, concentration, some potentials, etc. and so we can write,

$$X^\mu = \Delta x^\mu \quad \dots \quad (1)$$

The equation of entropy-generation is usually written as

$$\sigma = \Delta S_\nu = J_\mu X^\mu \quad (2)$$

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where σ is known as entropy-generation and is really the change ΔS_i of the entropy of system due to internal changes, J_μ is the flux corresponding to the generalised force X^μ, and the summation-convention, i.e., when the prefix and the suffix are same, it means summation over all possible values, has been used. After de Groot (1951), we shall consider the generalised forces as of a components linear vector, i.e., any linear combination of the forces, X^μ's, is also a generalised force. Then, as the consequence of the equation (2), the flux is also a vector. Of course, for general group of linear transformations, the generalised force is a contragradient vector and the flux a covariant vector. Thus if we consider a linear transformation of forces as

$$X^\mu = \beta_{\mu\nu}\, X'^\nu \qquad \dots \quad (3)$$

then the law of transformation of the fluxes is

$$J_\mu' = \beta_\mu{}^\nu\ J_\nu \qquad \dots \quad (4)$$

From the equations (1) and (2), we also get,

$$J_\mu = \frac{\partial S_\nu}{\partial x^\mu} \qquad (5)$$

Also from experience and also from simple physical considerations, we have,

$$J_\mu = f_\mu(X^\nu) \qquad \dots \quad (6)$$

where $f_\mu(X^\nu)$ denotes a functions of X^ν's (having finite continuous derivatives of first k-th order, k being a suitable number) with the usual conditions that at the equilibrium position, near about which all considerations are restricted, we have

$$X^\nu = 0, \quad J_\mu = 0 \ \text{ for all } \gamma\text{'s and } \mu\text{'s} \qquad (7)$$

LINEAR THEORY

For clear understanding of the present discussions, it appears that we should discuss the usual linear theory from the present stand point.

* Now, the equation (5) is only a form of the implicit assumption of perfect differentiability of the Pfaffian expression representing dS which deserves a close minute scrutiny. If equations (1), (2) and (7), which have been clearly pentioned by de Groot (1951) as facts of experience, are admitted, the Onsager reciprocal relation implies and is implied by the perfect differentiability of dS_i. If this fact is accepted to be valid in general, the entire theory becomes very simple. In the present deve- lopment, symmetries of higher order have been deduced esily and straightforwardly from this fact. But, the invariance of symmetry-relations of any order (if they exist) under the gneral group of linear transformations does not depend on this fact and follows generallY and directly from simple discussios of linear transformations as it can be seen here.

When the close neighbourhood of the equilibrium position, in which our consideration are restricted, is such that first approximation will suffice, from equation (6) we have

$$J_\mu = \frac{\partial J_\mu}{\partial x^\nu} \Delta x^\nu = L_{\mu\nu} X^\nu \quad \ldots \quad (8)$$

Then, from the relations (6), (7) and (8) we get

$$L_{\mu\nu} = \frac{\partial J_\mu}{\partial x^\nu} = \frac{\partial^2 S_t}{\partial x \partial x^\nu} = \frac{\partial^2 S_\nu}{\partial x^\nu \partial x^\mu} = \frac{\partial J_\nu}{\partial x^\mu} = L_{\nu\mu} \quad \ldots \quad (9)$$

If S satisfies the usual conditions of commutativity of the orders of partial differentiation. The relation

$$L_{\mu\nu} = L_{\nu\mu} \quad \ldots \quad (10)$$

is the usual reciprocal relation of Onsager.
Now from relations (3), (4) and (7), we have,

$$J'_\mu = \beta_\mu{}^\nu J_\nu = \beta_\mu{}^\nu L_{\nu\rho} X^\rho = \beta^\nu{}_\mu \beta^\rho{}_\lambda L_{\nu\rho} X' = L'_{\mu\lambda} X'^\lambda \quad \ldots \quad (11)$$

i.e.,

$$L'_{\mu\lambda} = L'_{\lambda\mu} \quad \ldots \quad (12)$$

Thus, from (10) and from the commutativity of $\beta_\mu{}^\nu$'s we get the invariance of symmetry-relation, viz,

$$L'_{\mu\lambda} = L'_{\lambda\mu} \quad \ldots \quad (13)$$

The relation (13) also shows that $L_{\mu\nu}$ is a covariant tensor of second order.

NON-LINEAR THEORY OF THE SECOND ORDER

When the neighbourhood of the equilibrium position is such that it is sufficient to retain terms of second order, we get, by Taylor's theorem after neglecting the error,

$$J_\mu = \frac{\partial J_\mu}{\partial x^\nu} \Delta x^\nu + \frac{1}{2!} \left\{ \frac{\partial^2 J_\mu}{\partial x^{\nu_1} \partial x^{\nu_2}} \Delta x^{\nu_1} \Delta x^{\nu_2} \right\}$$

$$= L_{\mu\nu} X^\nu + L_{\mu\nu_1\nu_2} X^{\nu_1} X^{\nu_2} \quad \ldots \quad (14)$$

where, when $\nu_1 \neq \nu_2$

$$L_{\mu\nu_1\nu_2} = \frac{\partial^2 J_\mu}{\partial x^{\nu_1} \partial x^{\nu_2}} = \frac{\partial^3 S_2}{\partial x^\mu \partial x^{\nu_1} \partial x^{\nu_2}}$$

$$= \frac{\partial^3 S_l}{\partial x^{\nu_1} \partial x^\mu \partial x^{\nu_2}} = \frac{\partial^2 J_{\nu_1}}{\partial x^\mu \partial x^{\nu_2}} = L_{\nu_1 \mu \nu_2},$$

$$= \frac{\partial^3 S_2}{\partial x^{\nu_2} \partial x^{\nu_2} \partial x^\mu} = \frac{\partial^2 J_{\nu_2}}{\partial x^{\nu_1} \partial^\mu} \quad L_{\nu_2 \nu_1 \mu}$$

and, when $\nu_1 = \nu_2 = \nu$,

$$L_{\mu\nu\nu} = \frac{1}{2!} \frac{\partial^2 J_\mu}{\partial x^\nu \partial x^\nu} = \frac{1}{2!} \frac{\partial^3 S}{\partial x^\mu \partial x^\nu \partial x^\nu}$$

$$= \frac{1}{2!} \frac{\partial^3 S}{\partial x^\nu \partial x^\mu \partial x^\nu} = \frac{1}{2!} \frac{\partial^2 J}{\partial x^\mu \partial x^\nu} = \frac{1}{2} L_{\nu\mu\nu}$$

$$= \frac{1}{2!} \frac{\partial^3 S}{\partial x^\mu \partial x^\nu \partial x^\mu} = \frac{1}{2!} \frac{\partial^2 J}{\partial x^\nu \partial x^\nu \partial x^\mu} = \frac{1}{2} L_{\nu_2\nu_1\mu}$$

provided S_f satisfies usual mathematical conditions of commutativity of orders of partial differentiation. Now, in expression (14), ν_1 and ν_2 are dummy suffices so commutatation ν_1 and ν_2 will lead to no new result. So, we have the symmetry relations of second orders as

$$L_{\mu\nu_1\nu_2} = L_{\nu_1\mu\nu_2} = L_{\nu_2\nu_1\mu} \qquad \dots \quad (15)$$

and

$$L_{\mu\nu\nu} = \tfrac{1}{2} L_{\nu\mu\nu} \qquad \dots \quad (16)$$

When there are only two generalised forces and so two fluxes, we have

$$L_{122} = \tfrac{1}{2} L_{212} = \tfrac{1}{2} L_{221},$$

$$L_{211} = \tfrac{1}{2} L_{121} = \tfrac{1}{2} L_{112}$$

Shrivastava and Kartar Singh (1966) was able to write these relations from some simple considerations.

As before, from (3) and (4) and (14) we obtain

$$L'_{\lambda\mu\nu} = \beta_\lambda{}^\sigma \beta_\mu{}^\sigma \beta_\nu{}^\tau L_{\rho\sigma\tau} \qquad \dots \quad (17)$$

From relations (15) and (16) and from the commutativity of $\beta_\mu{}^\nu$'s which are real numbers, we get invariance of the symmetric-relation. From (17) we also get that $L_{\lambda\nu\nu}$ is a covariant affine tensor of third order.

NON-LINEAR THEORY OF k TH ORDER

Now, when the neighbourhood about the equilibrium position is such that it will be sufficient to retain upto k th order say, by Taylor's theorem after neglecting the error after k-th team, we get

$$J_\mu = \frac{\partial J_\mu}{\partial x^\nu} \Delta x^\nu + \frac{1}{2!}\left(\frac{\partial^2 J_\mu}{\partial x^{\nu_1} \partial x^{\nu_2}} \Delta x^{\nu_1} \Delta x^{\nu_2}\right) + \dots + \frac{1}{k!}\left(\frac{\partial^k J_\mu}{\partial x^{\nu_1} \dots \partial x^{\nu_2}}\right) \Delta x^{\nu_1} \Delta x^{\nu_2} \dots \Delta x^{\nu_k}$$

$$= L_{\mu\nu} X^\nu + L_{\mu\nu_1\nu_2} X_{\nu_1} X_{\nu_2} + \dots + L_{\mu\nu_1 \dots \nu_k} X^\nu \dots X^{\nu_k} \qquad \dots \quad (18)$$

where

$$L_{\mu\nu_1 \dots \nu_k} = \frac{\pi_i \rho_i !}{\pi k!} \frac{\partial^k J_k}{\partial x^{\nu_1} \dots \partial x^{\nu_k}} \qquad \dots \quad (19)$$

where ρ_i is the number of the i th group of equal indices of the index set $\nu_1, \nu_2, \ldots \nu_k$. Now, as γ 's are dummy suffices, so no new result is obtained by interchanging them. So, we get symmetry-relations as

$$L_{\mu\nu_1\ldots\nu_k} = L_{\nu_1\mu\nu_2\ldots\nu_k} = \ldots = L_{\nu_k\nu_1\ldots\nu_{k-1}\mu}, \quad \nu_1 \neq \nu_2 \neq \ldots \neq \nu_k \quad \ldots \quad (20)$$

$$L_{\mu\nu_1\nu_1\nu_3\ldots\nu_k} = \frac{1}{2!}L_{\nu_1\mu\nu_1\nu_3\ldots\nu_k} = \ldots = L_{\nu_k\nu_1\nu_1\nu_3\ldots\mu}, \quad \nu_1 \neq \nu_3 \neq \ldots \neq \nu_k \quad (21)$$

$$L_{\mu\nu\nu\ldots\nu} = \frac{1}{k}L_{\nu\mu\nu\ldots\nu} = \ldots = \frac{1}{k}L_{\nu\nu\ldots\nu\mu}, \quad \nu_1 = \nu_2 = \ldots = \nu_k = \nu \quad \ldots \quad (22)$$

These are the symmetry-relations of k-th order. Proceeding as before, we have,

$$J'_\mu = \beta_\mu{}^\nu J_\nu = \beta_\mu{}^\nu[L_{\nu\rho}X^\rho + L_{\nu\rho_1\rho_2}X^{\rho_1}X^{\rho_2} + \ldots + L_{\nu\rho_1\ldots\rho_k}X^{\rho_1}\ldots X^{\rho_k}]$$

$$= \beta^\nu{}_\mu\beta^\rho{}_\sigma L_{\nu\rho}X'^\sigma + \beta^\nu{}_\mu\beta^\rho{}_{\sigma 1}\beta^\rho{}_{\sigma 2}L_{\nu\rho_1\rho_2}X'^{\sigma_1}X'^{\sigma_2} + \ldots + \beta^2{}_\mu\beta^{\rho_1}{}_{\sigma 1}\ldots\beta^{\rho_k}{}_{\sigma 1} L_{\nu\rho_1\ldots\rho_k}X'^{\sigma_1}\ldots X'^{\rho_k}$$

$$= L'_{\mu\sigma}X'^\sigma + L_{\mu\sigma_1\sigma_2}X^{\sigma_1}X^{\sigma_2} + \ldots + L'_{\mu\sigma_1\ldots\sigma_k}X'^{\sigma_1}X'^{\sigma_2}\ldots X'^{\sigma_k}$$

So we get

$$L'_{\mu\nu_1\ldots\nu_2} = \beta^\rho{}_\mu\beta^{\sigma_1}{}_{\nu_1}\beta^{\sigma_2}{}_{\nu_2}\ldots\beta^{\sigma_k}{}_{\nu_k}L_{\rho\sigma_1\ldots\sigma_k}, \quad j \leqslant k.$$

Arguing as in the preceeding cases, we have the invariance of the symmetry-relation of j-th order, $j \leqslant k$.

CONCLUDING REMARKS

From our above discussion, it is clear that if in phenomenological theories, we proceed from slightly altered assumption, which are also facts of experience, we get not only our present-day linear theory but also its generalisation upto any higher order. The mathematical method used is simple and straightforward.

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